INVESTIGATOR'S ANNUAL REPORT

National Park Service

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Reporting Year	Park
1999	Yellowstone

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Project Title (maximum 300 characters)
Effects of Snowmobile Use on Semi-Volatile Organic Compounds in the Yellowstone National Park Snowpack

Park-assigned Study #	Park-assigned Permit #	Permit Start Date	Permit Expiration Date

Study Starting Date	Estimated Study Ending Date
Jan 15, 1999	April 30, 2001

Study Status (*circle one*): Completed ~~Continuing~~ X Suspended Terminated before completed

Activity Type (*circle one*): ~~Research~~ Inventory Monitoring Education Other

Subject/Discipline (*circle one*):					
Agriculture	Ecology	Geo. Info. System (GIS)	Ichthyology	Recreation/ Aesthetics	Volcanology/
~~Air Quality~~	Entomology	Geochemistry	Integrated Pest Mgmt.	Restoration – Cultural	Geothermal
Anthropol./Ethnography	Environmental	Geohydrology	Invertebrates	Restoration – Natural	Water Quality
Archeology	Monitoring	Geology – Coastal	Limnology	Sedimentol./ Stratigraphy	~~Water Quantity~~
Botany	Erosion/ Sedimentation	Geology – Fluvial	Mammalogy	Social Science – Economics	Water Rights
Cave (Flora/ Fauna)	Exotic Sp. – Animals	Geology – General	Mgmt./ Administration	Social Science – Geography	Watershed Mgt.
Cave/ Karst	Exotic Sp. – Plants	Geology – Structural	Microbiology	Social Science – History	Wetlands
Climatology	Fire	Geomorphology	Minerals Management	Social Science – Sociology	Wildlife Management
Coastal/ Marine Systems	Fisheries Management	Geophysics	Oceanography	Social Science – Other	Zoology
Contaminants/ Haz. Mat.	Flood Mgmt./ History	Glaciology	Ornithology	Soil Science	
	Forestry	Herpetology	Paleontology	Tectonics	**Other**
	Fungi	Hydrology (Ground)	Petrology/ Mineralogy	Threat./ Endangrd Animals	
	Geo-Hazard (Chemical)	Hydrology (Surface)	Range Management	Threat./ Endangrd Plants	
	Geo-Hazard (Physical)				

Objectives (maximum 4000 characters)

The objective of this study has been to determine if semi-volatile organic compounds in the YNP snow pack and snow melt can be attributed to snowmobile traffic. In addition, it was desired to determine whether these compounds accumulate in the snow to levels which pose an environmental hazard and to provide a preliminary estimate of the extent of their persistence in the impacted area. Although EPA has designated polyaromatic hydrocarbons (PAHs) and other semi-volatile organic species as priority pollutants, there have been very few studies of these species in snow pack [6]. Consequently, this project has included development of reliable methods for sample collection and analysis of semi-volatile species from mobile sources in snow.

Findings and Status (maximum 4000 characters)

During the 1998-1999 winter season snow samples were collected at two sites. One site was located approximately 50 meters east of the West Entrance and 10 - 20 meters from the road and was selected because the nearby road has the highest concentration of snowmobile activity. The second site was located in the horse corral at the Tower Ranger Station because no recreational snowmobile traffic is permitted in this section of the park. Samples were taken from the wall of a freshly dug snow pit from each layer, as distinguished by snow structure, down to ground. Samples were placed in one gallon zip-sealable polyethylene bags which had been pre-rinsed three times with deionized (DI) water, once with 95% ethanol, and then air dried. Each bag held approximately

sample representative of the entire snow column at that site. Samples were collected weekly from January 15, 1999 through March 15, 1999 when the YNP snowmobile season ended.

Aerosol samples were also collected at both the West Entrance and the Tower Ranger Station during the 1998-1999 winter season. The total aerosol was sampled using a filter assembly. At the West Entrance a filter assembly was mounted on the air sampling hut just inside the gate. A similar filter assembly was mounted outside the horse barn at the Tower ranger station. Samples were taken weekly from Jan. 15 1999 through March 15, 1999. Aerosol was collected on 47 mm Millipore FALP Fluoropore filters. At the Tower site, total aerosol samples were collected for 7 day intervals. At the West Entrance, samples were collected for 3 – 4 day intervals. It was initially planned to sample for 7 day intervals at the West Entrance but the aerosol load was too high and the pressure drop across the filters became so large after 3 – 4 days that sampling had to be terminated. At the West Entrance, aerosol was also collected using a Graseby Anderson eight stage cascade impactor. The cascade impactor separates the aerosol particles by their aerodynamic diameters and impacts them onto aluminum substrates. The impactor samples were cut into sections and analyzed using imaging Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS). Filter samples were intended to be extracted and analyzed by GC-MS; however the analysis was not completed.

Additionally, during the 1998-1999 winter season, snow columns approximately three feet in height were constructed of eight-inch PVC irrigation piping. The columns were lined with teflon sheeting. The teflon sheeting was thoroughly cleaned with ethanol prior to lining the columns. Snow was weighed and added to the columns and then sprayed with a known quantity of dopant. The doped snow columns were placed in an undisturbed location near the well at the Tower Ranger Station in an attempt to determine whether contaminants were retained in the snowpack through the season. Columns were doped with either standard two-stroke engine oil dissolved in hexanes, a biodegradable two-stroke engine oil dissolved in hexanes, or snowmobile exhaust products which had been collected in a cold trap and suspended in hexanes. Two undoped columns were also prepared as controls. The columns were left to experience ambient conditions at the Tower Ranger Station and then returned to the laboratory for analysis after the onset of the major snowmelt.

Contamination levels in all of the samples and snow columns collected during the 1998-1999 winter season prevented accurate analysis of the samples. Before the sampling, the polyethylene bags used as sample containers were tested for extractable contaminants by placing one liter of nano-pure water in the bags for 72 hours at room temperature. This test was performed without precleaning the bags, as an assumed worst case scenario. It was considered that any contaminants would be more mobile in water and therefore more likely to extract into water than into snow. The water was subsequently analyzed using the same protocol used for samples and no contaminants were detected. Unfortunately, the mechanical and chemical interactions between the snow and the bags proved to differ significantly from that of the water. The snow samples were all contaminated with large amounts of steramide extrusion lubricants and phthalate plasticizers from the containers. These contaminants were at such high levels that they obscured detection and quantification of the analytes of interest. Apparently, the snow crystals physically scraped these contaminants from the surface of the sample bags.

Three of the West Yellowstone air filter samples were extracted by refluxing the samples for 16 hrs in 30 ml of methylene chloride. The extracts were then analyzed with GC/MS on a VG-70E-HS instrument. At the initial concentration, no analytes were detected. The samples were then concentrated by a factor of 10 by blow down with 99.999% nitrogen and reanalyzed. In the concentrated samples, several high molecular weight n-alkanes, including $C_{18}H_{38}$, $C_{20}H_{42}$, $C_{22}H_{46}$, and $C_{24}H_{50}$. Concentrations of these analytes were well below the ppbv level. The pressure drop across the filter samples taken in West Yellowstone at the end of sample acquisition was very high indicating that the pores had become blocked by high concentrations of particulate. This suggests that a large mass of aerosol was collected, even though few compounds were detected in the GC/MS analysis. The data suggests that we were unable to recover this material from the filters for analysis. ESCA analysis of the filter samples revealed that some of the organic material was not removed from the filters by the extraction process. However, additional extraction steps were also not successful in removing this organic material. A similar extraction procedure has been used successfully in our laboratory for the analysis of organic compounds in wood smoke. We suspect that the low concentrations of organic compounds found in the West Yellowstone samples

during the months between collection of the samples and analysis. Samples were stored in the dark at ambient temperature which could result in loss of organic compounds through evaporation and oxidation.

A cascade impactor sample collected at the West Entrance on Jan. 23 1999 was analyzed with TOF-SIMS and SEM[8]. This analysis is non-quantitative but provides qualitative assessment of the major components of the aerosol and their size distribution. Few, if any, particles greater than 5 microns in diameter were observed. In the 5 – 2.5 micron samples, evidence for ash and organic particulate was observed. The majority of particles observed were less than 2 microns in diameter. Two types of fine particles were observed in the SEM and TOF-SIMS images. One type of particle, somewhat "amoeba" shaped, seems to resemble the oil soot shown by McCrone and Delly in The Particle Atlas [4] except that it is covered by a film. X-ray microanalysis showed C, O, S, and a little K. A strong Al signal showed that the beam was penetrating the particle into the substrate. TOF-SIMS imaging of these same particles revealed that the surface was dominated by high molecular weight n-alkanes and bisulfate. Ion etching of the particles revealed inorganic cores which contained Na, K, Ca, and Fe. Another type of particle was evidenced only by a very thin black layer, which showed no elements (except background Al) by X-ray microanalysis. It appears that we can see these "black spots" in the SEM solely because they reduce the background Al signal from the substrate. Likely, then, the black spots are made of a light element which gives only a poor X-ray signal. These particles were readily erased by the electron beam. TOF-SIMS analysis of these same particles revealed that they were indeed composed predominantly of high molecular weight n-alkanes and were probably a varnish left on the surface by oil droplets.

Additional impactor samples taken at the West Entrance were not analyzed because of the expense of the analysis.

Reports Produced (Reference Title, Authors, Name of Publication, Abstract, Volume and Page Numbers, Year Published, Type of Reference, Keywords)

Single Particle Analysis of Particulate Pollutants in Yellowstone National Park During the Winter Snowmobile Season, R.E. Peterson and B.J. Tyler, In. Secondary Ion Mass Spectrometry (SIMS XII) Eds. A. Benninghoven, P. Bertrand, H.N. Migeon, H.W. Werner, pg. 985-988, Elsevier, 2000, Conference Proceedings,

For this study, were one or more specimens collected and removed from the park but not destroyed during analysis? (Y/N) No
If "Yes", where are the specimens currently stored?

Funding provided this reporting year by NPS (enter dollar amount)	Funding provided this reporting year by other sources (enter dollar amount)
$ 10,000	$ 35,000

List other U.S. Government Agencies supporting this study and funding each provided this reporting year:
NSF

Fill out the following ONLY IF the National Park Service supported this project in this reporting year by providing money to a university or college

Full name of college or university	Name of department or program
Montana State University	Dept. of Chemical Engineering
Name of campus, if unique	Annual funding provided by NPS to university or college this reporting year
Bozeman	$ 10,000